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Characterization of Interphases Between PMDA/4-BDAF
Polyimides and Silver Substrates Using Surface-Enhanced
Raman Scattering and Reflection-Absorption Infrared
Spectroscopy

by

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Characterization of Interphases Between PMDA/4-BDAF Polyimides and Silver Substrates Using Surface-Enhanced Raman Scattering and Reflection-Absorption Infrared Spectroscopy

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ABSTRACT

Surface-enhanced Raman scattering (SERS) and reflection-absorption infrared spectroscopy (RAIR) were used to determine the molecular structure of interphases formed by curing the polyamic acid of pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF) against silver substrates. SERS spectra of the cured polymer were more similar to the SERS spectra of the polyamic acid than to the normal Raman spectrum of the polyimide, indicating that curing of the polymer was inhibited by interaction of the polyamic acid with the substrate. Thus, the strongest band in the normal Raman spectrum of the polyimide was near 1406 cm^{-1} and was assigned to the CNC axial stretching mode. The next strongest band was near 1802 cm^{-1} and was assigned to the C=O stretching mode of the imide groups. The strongest band in the SERS spectrum was near 1609 cm^{-1} and was attributed to the ring stretching mode ν(8a). Bands due to the CNC axial stretching mode and the C=O stretching mode were relatively weak. These conclusions were substantiated by results obtained from RAIR spectra of thin films of the polyamic acid of PMDA/4-BDAF cured against thick silver films. RAIR spectra obtained before and after curing relatively thick films of the polyamic acid spin-coated onto silver substrates were similar to transmission infrared spectra of neat polyamic acid and polyimide. However, RAIR spectra obtained after curing relatively thin films of polyamic acid spin-coated onto silver substrates were characterized by weak bands attributed to the imide C=O and axial CNC stretching modes and by the presence of

bands assigned to residual amide and carboxylate groups, verifying that imidization was inhibited by interaction of the polyamic acid with the substrate.

I. Introduction

Polyimides are widely used as adhesives, dielectrics in microelectronics, and as matrix materials in composite materials. As a result, there has been considerable interest in the mechanisms by which polyimides interact with substrates such as metals and graphite. Much of this work has concerned the structure of interfaces between metals and polyimides derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA).

Numerous investigations of metal-on-polyimide interfaces have been reported (1-12). It has generally been observed that metals such as aluminum and chromium, which have strongly negative free energies of vapor phase oxidation, form an interfacial oxide with the carbonyl oxygen atoms on the polyimide. However, other metals such as copper and nickel interact only weakly with PMDA/ODA polyimides and tend to diffuse into the polymer during deposition rather than react with functional groups on the surface (2, 4).

Polyimide-on-metal interfaces have not been so widely studied. This type of interface can be formed by spin-coating a polyamic acid onto a metal surface and then curing it to form the polyimide or by codepositing monomers of the polyimide onto metal surfaces and then curing.

Kim et al (13, 14) used transmission electron microscopy (TEM) to investigate interfaces formed by thermal curing of polyamic acid spin-coated onto copper substrates. Cross-section TEM results showed that very fine copper-rich particles were distributed in the polyimide. However, particles were not found

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closer than 80-200 nm from the copper surface. It was suggested that the polyamic acid precursor reacted with copper to form a polyamic acid complex which decomposed during subsequent thermal curing, resulting in the formation of copper-rich particles in the polyimide.

Burrell et al (15) utilized XPS and IR to investigate thin films of polyimide prepared by spin-coating polyamic acids onto copper and aluminum substrates, followed by the thermal treatment to promote imidization of the film. Films prepared on Al substrates were completely cured during the heat treatment, as shown by XPS and IR measurements. Upon curing, the peaks near 284.6 and 286.0 eV in the C(1s) spectra of polyamic acid which were assigned to carbon bound to other carbons or hydrogen and carbon bound to oxygen and nitrogen, respectively, appeared sharper in the C(1s) spectra of the polyimide film. Peaks near 287.9 and 289.0 eV due to carbonyl carbon in amide and acid groups merged into a single carbonyl component near 288.6 eV after thermal curing. The O(1s) spectra showed a decrease in intensity of the C-O component relative to the C=O component. N(1s) spectra showed the appearance of a peak near 400.6 eV due to imide and the disappearance of a peak near 399.9 eV due to amide in polyamic acid. These observations indicated the formation of polyimide films on Al substrates. Grazing angle reflectance infrared spectra were characterized by bands near 1780 and 1730 cm^{-1} which were assigned to imide groups, supporting the conclusions obtained from the XPS investigation.

In the case of polyimide/copper interfaces, the C(1s) spectra exhibited several carbonyl components which were not related to the cured polyimide. The peak near 399.9 eV associated with the amide groups was still observed in N(1s) spectra. Peaks due to Cu(I) and Cu(II) were both present in the Cu(2p) spectra. In the infrared spectra of the polyimide on copper substrates, the band characteristic of imide functionality near 1730 cm^{-1} was not observed. Instead a broad band near 1650 cm^{-1} was observed which was attributed to the superposition of the amide carbonyl band and one or more bands due to new chemical species. Another new band indicative of cuprous oxide was also observed near 640 cm^{-1}. As a result, it was proposed that copper/polyamic acid complexes were formed when polyamic acids were deposited onto copper substrates. A portion of these complexes was able to react with the amide group to yield imide groups plus oxide during thermal curing. However, formation of the copper/polyamic acid complex prevented films from curing completely during thermal treatment.

Grunze and Lamb (16, 17) used XPS to investigate vapor deposition of PMDA and ODA onto polycrystalline silver surfaces. PMDA and ODA were both chemisorbed on the silver surface through the oxygen atoms in the PMDA and ODA fragments. Co-deposition of PMDA and ODA followed by thermal treatment of the films led to formation of thermally stable polyimide films. Peaks were observed near 286.2, 286.9, and 290.0 eV in the C(1s) spectra of co-deposited PMDA/ODA films having a thickness of about 11 A. These peaks were assigned to aromatic carbon in the ODA, carbon

in the PMDA ring and carbon attached to the nitrogen or oxygen in ODA, and carbonyl carbon, respectively. The calculated intensity ratio of these peaks was 4.9.5:9.6, while the ratio for a stoichiometric PMDA/ODA polyimide was 4:10:8. The relatively high intensity of the low binding energy C(1s) peak near 286.2 eV was explained by the presence of fragmented PMDA and ODA in the polyimide/silver interface. Contributions of fragmented PMDA and ODA to the spectra of the thin film were also evident in the O(1s) spectra where a peak near 531.5 eV was attributed to oxygen bonded directly to the silver surface. Therefore, it was concluded that the adhesion of polyimide films to silver surfaces involved bonding to fragments of PMDA and ODA which were chemisorbed on the silver surface.

Several papers have appeared in which the structure of interfaces between metals and model compounds for PMDA/ODA polyimides was described. Rossi et al (18) carried out molecular orbital calculations on complexes of Cr and N,N'-diphenyl pyromellitic diimide, a model compound for PMDA/ODA polyimide. Their results indicated that Cr was located above the central benzene ring to form a complex at the initial deposition of Cr.

Ramsier and Henriksen reported inelastic electron tunneling spectra (IETS) of phthalimide (PIMH) and N-phenyl phthalimide (PIMPh) adsorbed onto aluminum oxide in tunnel junction structures (19). They reported that upon adsorption, the CH stretching modes of the rings in PIMH were shifted to lower frequencies, implying there was a strong interaction between the rings and the substrate and that the rings were mostly parallel

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to the substrate. In the case of PIMPh it was noted that several bands characteristic of the rings were shifted toward even lower frequencies by between 8 and 25 cm^{-1}, indicating a stronger interaction between the rings and the substrate for PIMPh than for PIMH. In both cases, a band was observed near 411 cm^{-1} and attributed to formation of an Al-N complex. It was suggested that PIMH and PIMPh are both adsorbed by bonding between the lone pair of electrons on the nitrogen atoms with Lewis acid sites (Al cations). It was also suggested that intermolecular hydrogen bonding occurred which modified the N-H and C=O stretching modes.

We have recently applied surface-enhanced Raman scattering (SERS) to the non-destructive characterization of polymer/metal interfaces. SERS is a phenomenon in which the Raman scattering cross section of molecules adjacent to the roughened surfaces of certain metals is enhanced as much as 10^6 compared to its value for normal Raman scattering. The enhancement for molecules more than a few molecular layers from the metal surface is negligible. Since the enhancement for molecules adjacent to the surface is so great, SERS is surface-selective and can be used for non-destructive characterization of polymer/metal interphases.

Boerio et al (20) used SERS to determine the molecular structure of interphases formed when a model acrylic adhesive was cured against silver island films. They found that o-benzoic sulfimide (saccharin), a component of the cure system, reacted with the metal surface to form a salt. Formation of the salt was an important step in curing the adhesive since the metal ions in

the salt catalyzed decomposition of a peroxide which initiated polymerization of the acrylic monomer.

Tsai et al used surface-enhanced Raman scattering (SERS) to investigate the adsorption of imides onto silver substrates (21). They observed considerable differences between normal Raman and SERS spectra of phthalimide (PIMH) and pyromellitic diimide (PMDI). The carbonyl stretching modes were very strong in the normal Raman spectra but were weak in the SERS spectra. However, bands related to the axial CNC stretching mode and to a CX stretching mode of the benzene rings were strong in both normal Raman and SERS spectra of PIMH and PMDI, indicating that PIMH and PMDI were both adsorbed with a vertical configuration in which the carbonyl groups were parallel to the surface. A new band was observed near 690 cm^{-1} in SERS spectra and attributed to the CNC deformation mode shifted upward by ionization of the imide nitrogen. It was concluded that both PIMH and PMDI were adsorbed onto silver with an end-on configuration by dissociation of the imide hydrogen.

Considerably different results were obtained for N-phenyl phthalimide (PIMPh) and N,N-diphenyl pyromellitic diimide (PMDIPh). Bands assigned to carbonyl stretching modes were strong in normal Raman and SERS spectra of both compounds, indicating that PIMPh and PMDIPh were adsorbed onto silver edge-on with the carbonyl groups perpendicular to the surface or with no preferred orientation (21).

The polyimide prepared from pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF)

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has potential applications as a sizing agent for graphite fibers in advanced composites and as an erosion-resistant coating for composites. However, little is known regarding the effect that inorganic substrates have on the molecular structure of this polyimide.

The purpose of this paper is to present results obtained using surface-enhanced Raman scattering (SERS) to determine the molecular structure of the interphase between PMDA/4-BDAF polyimide and silver substrates. A subsequent paper will describe interfaces between PMDA/4-BDAF polyimide and graphite substrates. The strongest band in the normal Raman spectrum of the polyimide was near 1410 cm^{-1} and was assigned to the CNC axial stretching mode of the imide rings whereas the strongest band in the SERS spectrum of the polyimide cured against silver was near 1610 cm^{-1} and was assigned to a combination of carboxylate stretching and mode ν(8a) of the substituted benzene rings. The low intensity of the band near 1410 cm^{-1} and the great intensity of the band near 1610 cm^{-1} in SERS spectra indicated that the curing reaction was inhibited by the substrate. These conclusions were substantiated by results obtained from reflection-absorption infrared (RAIR) spectroscopy.

II. Experimental

Samples were prepared for SERS investigations as described below. Glass slides were immersed in 0.1N NaOH and in 0.1N HCl aqueous solutions for one hour. The slides were then rinsed in distilled-deionized water, blown dry with nitrogen, cleaned

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ultrasonically in absolute ethanol several times, and blown dry with nitrogen again.

The glass slides were placed in a vacuum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Silver wire was wrapped around a tungsten filament which was slowly heated resistively to evaporate island films onto the glass substrates at a rate of about 1 A/sec. A quartz crystal oscillator thickness monitor was used to control the thickness of the island films at about 40 A.

The polyamic acid of pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF) was obtained from Ethyl Corporation. Thin films were deposited on the silver island films by spin-coating from solutions in N-methyl pyrrolidone (NMP). The films were cured by heating at $107^{\circ}C$ for 15 minutes and at $200^{\circ}C$ for an additional 15 minutes in an oven purged with argon.

SERS spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The slit settings of the monochromator provided a spectral resolution of 10 cm^{-1} for the SERS spectra. The green line of the laser (5145 angstroms in wavelength) was incident on the sample at an angle of about 65° relative to the normal of the sample surface for SERS experiments and was s-polarized. Scattered light was collected using an f/0.95 collection lens and focused onto the entrance slits of the monochromator. Spectra were obtained using a scan speed of 50

cm^{-1} per minute and time constant of either 2 or 10 seconds. Plasma lines were removed from the spectra by the placement of a narrow-bandpass filter between the laser and sample. In many of the spectra, a considerable background, which was removed by zero suppression, was observed.

Normal Raman spectra were obtained from a small amount of powdered sample supported in a glass capillary tube using the instrument described above. All of the instrumental parameters were the same as used for the SERS spectra except that the slits were set for a spectral width of 5 cm^{-1}.

The thickness of the polyamic acid films deposited on the silver island films was determined by ellipsometry. Thick (several hundred angstroms) films of silver were evaporated onto glass slides. Films of PMDA/4-BDAF were spun onto the silver mirrors from the same solutions and at the same speeds as were used to prepare the SERS samples. The thickness of the films was measured using a Rudolph Research Model 436 ellipsometer to examine the silver substrates before and after deposition of the organic films.

Similar techniques were used to obtain reflection-absorption infrared spectra of PMDA/4BDAF films on silver substrates. Thick films of silver were evaporated onto glass slides and films of the polyamic acid were spin-coated onto the silver. Infrared spectra of the films were obtained using a Perkin-Elmer Model 1800 Fourier-transform infrared (FTIR) spectrophotometer and external reflection accessories provided by Harrick Scientific Co. Transmission infrared spectra were obtained using the same

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spectrophotometer. Samples were prepared by mixing a small amount of powdered sample with potassium bromide powder and then pressing the mixture into a clear pellet under high pressure.

Some Raman spectra were acquired using a detection system consisting of a Stanford Research Model 400 gated photon counter interfaced to a Hewlett-Packard Vectra computer. In that case the scan rate was about 65 cm^{-1}/min. However, the other instrumental parameters were similar to those described above.

III. Results and Discussion

The molecular structure of the polyamic acid and polyimide of PMDA/4-BDAF are shown in Figure 1. Normal Raman spectra of the polyamic acid and polyimide are shown in Figure 2 while the observed bands and preliminary band assignments are summarized in Table I. The normal Raman spectrum of the polyamic acid was characterized by a strong band near 1623 cm^{-1} and by medium intensity bands near 1691, 1577, 1341, 1180, 941, and 765 cm^{-1} (see Figure 2A). The band near 1623 cm^{-1} was attributed to mode $\nu(8a)$ of the benzene rings while those near 1691 and 941 cm^{-1} were assigned to the C=O stretching and OH out-of-plane bending modes of the acid groups, respectively. Bands near 1577 and 1341 cm^{-1} were attributed to modes of the amide groups while the band near 1180 cm^{-1} was assigned to $\nu(13)$, a CH in-plane bending mode of the C_6H_2 ring. When the polyamic acid of PMDA/4-BDAF was cured, bands near 1691, 1577, and 1341 cm^{-1} disappeared and bands which were assigned to the C=O and CNC axial stretching modes of imide groups appeared near 1802 and 1406 cm^{-1}, indicating that imidization had occurred (see Figure 2B).

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Transmission infrared spectra of the polyamic acid of PMDA/4-BDAF before and after curing are shown in Figure 3 and the observed bands are summarized in Table II. Spectra of the polyamic acid before curing were characterized by strong bands near 1724, 1667, 1610, 1503, 1246, 1205, and 1175 cm^{-1} and by weaker bands near 1779, 1545, and 1408 cm^{-1} (see Figure 3A). Bands near 1779 and 1724 cm^{-1} were assigned to C=O stretching modes of imide groups, indicating that the polyamic acid was partially imidized. The strong, broad band near 1667 cm^{-1} and the weak band near 1545 cm^{-1} were attributed to the amide I and II modes. Strong bands near 1503 cm^{-1} and 1174 cm^{-1} were assigned to the modes ν(19a) and ν(13) of the C_6H_4 and C_6H_2 rings, respectively. Strong bands near 1246 and 1205 cm^{-1} were assigned to the COC asymmetric stretching and symmetric CF_3 stretching modes of the 4-BDAF moieties, respectively. When the polyamic acid was cured, the bands near 1667, 1545, and 1408 cm^{-1} disappeared while the bands near 1779 and 1728 cm^{-1} increased in intensity and a new band assigned to the axial CNC stretching mode of the imide groups appeared near 1379 cm^{-1}, indicating that imidization had occurred (see Figure 3B).

SERS spectra of the polyamic acid of PMDA/4-BDAF are shown in Figure 4 while the observed bands and assignments are summarized in Table I. SERS spectra of the polyimide are also shown in Figure 4 while the observed bands and assignments are summarized in Table II. The SERS spectrum of the polyamic acid was characterized by strong bands near 1621, 1346, and 1181 cm^{-1} and by weaker bands 1578, 1421, and 738 cm^{-1} (see Figure 4A).

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The band near 1621 was attributed to a combination of the ring mode $\nu(8a)$ and $\nu_a(COO^-)$, the asymmetric stretching mode of the carboxylate groups, while that near 1181 cm^{-1} was assigned to the mode $\nu(13)$ of the C_6H_2 moieties. Bands near 1578 and 1421 cm^{-1} were assigned to the amide II mode and to $n_s(COO^-)$, the symmetric carboxylate stretching mode, respectively. The strong band near 1346 cm^{-1} was attributed to the CN stretching mode.

After curing at 107°C for 15 minutes and at 200°C for an additional 15 minutes in an argon-purged oven, the SERS spectra changed significantly (see Figure 4B). The band near 1346 cm^{-1} decreased in intensity while a new band assigned to the CNC axial stretching mode of imide groups appeared near 1410 cm^{-1}. The band near 1621 cm^{-1} decreased in frequency to approximately 1609 cm^{-1} and a new band assigned to the C=O stretching mode of imide groups appeared near 1797 cm^{-1}. Broad, weak bands also appeared near 1706 and 1250 cm^{-1}.

It should be noted that longer cure times had no effect on the SERS spectra. As a result, only the results for the shortest cure times are shown here. It should also be noted that reflection-absorption infrared spectra obtained from thin films of polyamic acid spin-coated onto thick silver films and then cured at 107°C for 15 minutes and at 200°C for an additional 15 minutes in an argon-purged oven showed that this cure procedure resulted in virtually complete conversion of polyamic acid to polyimide (see below).

SERS spectra of the cured polyimide resembled SERS spectra of the polyamic acid more than normal Raman spectra of the

polyimide. Thus, the strongest band in the SERS spectrum of the polyimide was near 1609 cm^{-1} although the strongest band in the normal Raman spectrum of the polyimide was near 1406 cm^{-1}. The band due to the C=O stretching mode near 1802 cm^{-1} was relatively strong in the normal Raman spectrum of the polyimide but was weak in the SERS spectrum of the polyimide and absent from the SERS spectrum of the polyamic acid. These results undoubtedly indicate that curing of the polyamic acid films adjacent to the substrate was inhibited by interaction of carboxylate groups of the polyamic acid with the oxidized surface of the substrate.

Some additional differences were observed between the SERS and normal Raman spectra of the polyimide. For example, a weak band was consistently observed near 1706 cm^{-1} in the SERS spectra which was not observed in the normal Raman spectra. We have observed a very similar band near 1690 cm^{-1} in the SERS spectra of PMDA/ODA polyimide (22). This band may be related to isoimide species or to residual amide or acid groups in the cured films.

Results obtained from x-ray photoelectron spectroscopy indicate that isoimides are observed in the interphase when the polyamic acid of PMDA/4-BDAF is cured against silver as was done here (23). Bands related to isoimide species have been observed previously in infrared spectra of polyimides. For example, Buchwalter and coworkers observed a band near 1800 cm^{-1} in infrared spectra of PMDA/ODA polyimides which they assigned to isoimide (24). Painter and coworkers synthesized a model polyamic acid from PMDA and p-anisidine and showed that when ring closure was achieved chemically in acetic anhydride using

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pyridine as catalyst, strong bands assigned to isoimide species appeared near 1700 and 1800 cm^{-1} (25). In the absence of the catalyst, ring closure in acetic anhydride resulted in imide formation characterized by bands near 1720 and 1780 cm^{-1}. Perhaps the only previous observation of the Raman spectra of an isoimide was by Wunder (26) who obtained Fourier-transform Raman spectra of several polyimides and assigned a band near 1800 cm^{-1} to isoimide species.

In an effort to resolve the assignment of the band near 1706 cm^{-1} in SERS spectra of the PMDA/4-BDAF polyimide, a model compound similar to that described by Painter et al was synthesized by reacting PMDA with aniline to form an amic acid. The synthesis was carried out by slowly adding aniline to PMDA (2:1 mole ratio) in NMP at room temperature. After stirring the mixture for 24 hours, the amic acid was precipitated by adding distilled water. A 1:1 mixture of acetic acid and pyridine was then added to a solution of the amic acid in NMP to chemically cure the amic acid. As indicated earlier, Painter et al found that chemically curing their model compound resulted in the formation of isoimide moieties with characteristic infrared absorption bands near 1700 and 1800 cm^{-1} (25). Thermal curing resulted in formation of the imide with characteristic bands near 1720 and 1780 cm^{-1} (25).

When the amic acid of PMDA and aniline was cured thermally, N, N-diphenyl pyromellitic diimide (DPPMDI) was obtained with characteristic infrared absorptions near 1725 and 1784 cm^{-1}. However, when the amic acid was cured chemically, an isoimide

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with infrared absorptions near 1712 and 1807 cm^{-1} was obtained. Moreover, a strong band was observed near 1704 cm^{-1} in the Raman spectrum of the chemically cured compound and attributed to the isoimide. Based on these results, the band near 1706 cm^{-1} in the SERS spectra of the PMDA/4-BDAF polimide was assigned to isoimide moieties.

An alternative interpretation based on the results of Grunze is possible, however. Grunze et al (27) obtained XPS and RAIR spectra of PMDA and ODA adsorbed from the vapor phase onto silver and copper. The XPS spectra of PMDA adsorbed onto silver showed a deficit of one carbonyl group per PMDA molecule, indicating that PMDA was adsorbed dissociatively through the anhydride groups. When PMDA was adsorbed onto copper, the XPS results showed additional decomposition involving loss of two carbonyl groups per molecule. Bands related to the anhydride group modes were observed in the RAIR spectra but those related to the phenyl group modes were weak or missing entirely, possibly indicating fragmentation of the phenyl rings. A new band, tentatively assigned to a formate-like species, was observed near 1703 cm^{-1} that was not observed for bulk PMDA. It is possible that the band near 1706 cm^{-1} in our SERS spectra of PMDA/4-BDAF is related to that near 1703 cm^{-1} in the RAIR spectra of PMDA/ODA obtained by Grunze et al. However, the best evidence available at this time is that the band near 1706 cm^{-1} is related to isoimide.

Reflection-absorption infrared spectra were obtained before and after curing of films of polyamic acid spin-coated onto thick silver films from solutions of varying concentration in N-

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methylpyrrolidone (see Figures 5-7). The bands observed in the RAIR spectra of the polyamic acids are summarized in Table I while those observed in the spectra of the polyimides are summarized in Table II. Generally speaking, the RAIR spectra obtained from these films before curing were similar to transmission spectra of the bulk polyamic acid. RAIR spectra obtained from films spin-coated onto silver films from 5% solutions in NMP and then cured in an argon-purged oven at $107^{O}C$ for 15 minutes and at $200^{O}C$ for an additional 15 minutes were also similar to transmission spectra of the bulk cured polyimide. These spectra were characterized by a strong band near 1730 cm^{-1} and by a weak band near 1780 cm^{-1} which were assigned to the C=O stretching modes of imide groups (see Figure 5). No bands characteristic of the amide or acid groups of the polyamic acid were observed in these spectra, indicating that complete imidization had occurred.

However, RAIR spectra obtained from films of the polyamic acid spin-coated onto silver from solutions in NMP having concentrations of 1% and 0.2% and then cured at $107^{O}C$ for 15 minutes and at $200^{O}C$ for an additional 15 minutes in an argon-purged oven were significantly different from transmission spectra of the bulk polyimide. Differences between the RAIR spectra of cured films on silver and transmission spectra of the bulk cured polyimide were especially significant for films spin-coated onto silver from solutions having concentrations of 1% and 0.2%. For example, the intensity of the band near 1380 cm^{-1}, which was assigned to the axial CNC stretching mode of the imide

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groups, decreased relative to that of the band assigned to ring mode ν(19a) near 1500 cm^{-1} as the concentration of the solutions from which the films were spun onto the thick silver films was decreased. For films spun onto silver from 5%, 1%, and 0.2% solutions in N-methylpyrrolidone and then cured, the ratio of the intensity of the band near 1380 cm^{-1} to that near 1500 cm^{-1} was 0.38, 0.25, and 0.11, respectively (see Figure 8).

The decrease in the ratio of the intensity of the bands near 1380 and 1500 cm^{-1} could be due to an orientation effect or to decreased imidization for the thinnest films spin-coated from the most dilute solutions. It is well known that RAIR spectroscopy is very sensitive to the preferential orientation of functional groups at the surface of a metal and that vibrational modes having transition moments perpendicular to the surface of the substrate appear with much greater intensity than do vibrations having transition moments parallel to the substrate surface. However, orientation effects are not considered to account for the gradual decrease in the intensity of the band near 1380 cm^{-1} in the RAIR spectra of PMDA/4-BDAF polyimide as the film thickness is decreased. Most likely, the decrease in intensity of the band near 1380 cm^{-1} as the film thickness was decreased was related to inhibition of imidization by the surface.

Support for this interpretation was obtained from the RAIR spectra of the polyamic acid films spin-coated onto the thick silver films from solutions having a concentration of 0.2%. Before curing, bands related to the amide I and II modes were observed near 1667 and 1545 cm^{-1} (see Figure 7A). These bands

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were clearly observed after curing (see Figure 7B), indicating that curing was inhibited adjacent to the metal surface.

The intensity of the band near 1728 cm^{-1}, which was attributed to the C=O stretching mode, also decreased relative to that of the band near 1500 cm^{-1}. The relative intensity of these bands was 0.98, 0.71, and 0.59 for films spin-coated onto silver from solutions having concentrations of 5%, 1%, and 0.2% (see Figure 8). These changes were also probably due to cure inhibition by the surface.

In order for the decrease in intensity observed for the bands near 1728 and 1380 cm^{-1} to be due to orientation effects, it would be necessary for the transition moments of both modes to be parallel to the surface. Since these bands are assigned to the CNC axial stretching and C=O stretching modes, both transition modes can be parallel to the surface only when the C_6H_2 rings of the PMDA moieties are parallel to the surface. However, the great intensity of the band near 1500 cm^{-1}, which was assigned to the ring mode $\nu(19a)$, indicated that the rings were not parallel to the surface.

The picture that emerges from the RAIR spectra of the thin polyamic acid films spin-coated onto thick silver films is that the C_6H_2 rings were perpendicular to the surface and that some of the acid groups interacted with the oxide to form carboxylate groups. This picture is, of course, consistent with that obtained from SERS and by Grunze (16, 17, 27).

IV. Conclusions

Surface-enhanced Raman scattering (SERS) is a powerful technique for non-destructive characterization of polymer/metal interphases. Results obtained from SERS showed that the molecular structure of interphases formed by curing the polyamic acid of pyromellitic dianhydride (PMDA) and 2,2-bis[4-(4-aminophenoxy)-phenyl]-hexafluoropropane (4-BDAF) against silver substrates was considerably different than the bulk structure of the polyimide. SERS spectra obtained from films of the polyamic acid cured against silver substrates were more similar to the SERS spectra of the polyamic acid than to normal Raman spectra of the polyimide, indicating that curing of the polymer was inhibited by interaction of the polyamic acid with the substrate. Thus, the strongest band in the normal Raman spectrum of the polyimide was near 1406 cm^{-1} and was assigned to the CNC axial stretching mode. The second strongest band was near 1802 cm^{-1} and was assigned to the C=O stretching mode of the imide groups. However, the strongest band in the SERS spectrum of the polyimide was near 1609 cm^{-1} and was attributed to the ring stretching mode $\nu(8a)$. Bands due to the CNC axial stretching mode and the C=O stretching mode were relatively weak. The band due to $\nu(8a)$ was also the strongest band in the SERS spectra of the polyamic acid.

RAIR spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF cured against thick silver films substantiated the conclusion that curing was inhibited by the substrate. RAIR spectra obtained before and after curing relatively thick films of the polyamic acid spin-coated onto silver substrates were

similar to transmission infrared spectra of neat polyamic acid and polyimide. However, RAIR spectra obtained after curing relatively thin films of polyamic acid spin-coated onto silver substrates were characterized by weak bands attributed to the imide C=O and axial CNC stretching modes and by the presence of bands assigned to residual amide and carboxylate groups, verifying that imidization was inhibited by interaction of the polyamic acid with the subst·ate.

V. Acknowledgements

VI. References

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Table I. Tentative assignments of normal Raman, SERS, infrared and RAIR spectra from uncured L-30N.

Frequency (cm^{-1})

NR	SERS	IR	RAIR	Tentative Assign.
1691(M)		1724(M)	1723(M)	ν(C=O)-acid
		1667(M)	1663(M)	ν(C=O)-amide I
1623(S)				ν(8a)-C_6H_2 & C_6H_4
	1621(S)	1610(M)	1608(M)	ν_a(COO$^-$)+ν(8a)-rings
1577(M)	1578(M)	1545(W)	1542(M)	β(NH)-amide II
		1503(S)	1502(S)	ν(19a)-C_6H_4
	1421(W)			ν_s(COO$^-$)
		1408(M)	1410(W)	ν_s(COO$^-$)+ν(CN)-amide
1341(M)	1345(M)			ν(CN)-amide III
		1301(W)	1301(W)	ν(CO)+β(OH)-acid
		1246(S)	1248(S)	ν_a(COC)-ODA+ν_a(CF$_3$)
		1205(M)	1206(M)	ν_s(CF$_3$)
1180(M)	1181(M)	1174(S)	1172(M)	ν(13)-C_6H_2
1020(W)		1016(W)	1017(W)	ν(18a)-C_6H_2
		968(W)		ν(17a)-C_6H_4
941(M)		929(W)		π(OH)-acid
		875(W)		ν(17b)-C_6H_2
853(W)				ν(1)-C_6H_2
765(M)		746(W)		β(C=O)-acid
735(W)	738(W)	736(W)		ν(1)-C_6H_4
		662(W)		π(C=O)-acid
629(W)		612(W)		ν(6b)-C_6H_4

S: strong, M: medium, W: weak
s: symmetric, a: antisymmetric

Table II. Tentative assignments of normal Raman, SERS,
infrared and RAIR spectra from cured L-30N.

Frequency (cm^{-1})

NR	SERS	IR	RAIR	Tentative Assign.
1802(S)	1801(M)	1779(W)	1780(W)	ν(C=O),in-phase
				}imideI
		1728(S)	1730(M)	ν(C=O),out-of-phase
	1706(W)			ν(C=N)-isoimide
1623(M)				ν(8a)-C_6H_2
	1609(S)		1608(M)	ν_a(COO$^-$)+ν(8a)-rings
1600(W)			1600(W)	ν(8a)-C_6H_4
			1546(W)	β(NH)-amide II
		1504(S)	1502(S)	ν(19a)-C_6H_4
		1456(W)		ν(19b)-C_6H_2
	1421(W)		1410(W)	ν_s(COO$^-$)+ν(CN)-amide
1406(S)	1409(W)	1379(S)	1380(W)	ν(CNC),axial-imide II
	1345(W)			ν(CN)-amide III
		1248(S)	1250(S)	ν_a(COC)-ODA+ν_a(CF$_3$)
		1207(M)	1209(M)	ν_s(CF$_3$)
1180(M)	1181(M)	1176(S)	1178(M)	ν(13)-C_6H_2
1134(W)		1116(M)	1116(W)	ν(CNC),trans.-imideIII
		1093(W)	1095(W)	ν(13)-C_6H_2
		1017(W)		ν(18a)-C_6H_2
		968(W)		ν(17a)-C_6H_4
		881(W)		ν(17b)-C_6H_2
853(W)				ν(1)-C_6H_2
		823(W)	825(W)	ν(17b)-C_6H_4
732(W)		726(W)	727(W)	CNC,o.p.b-imide IV
		704(W)		ν(12)-C_6H_4
627(W)	631(W)			i.p.b. of imide
		608(W)		ν(12)-C_6H_2

S: strong, M: medium, W: weak
s: symmetric, a: antisymmetric, trans.: transverse
i.p.b.: in-plane bending, o.p.b.: out-of-plane bending
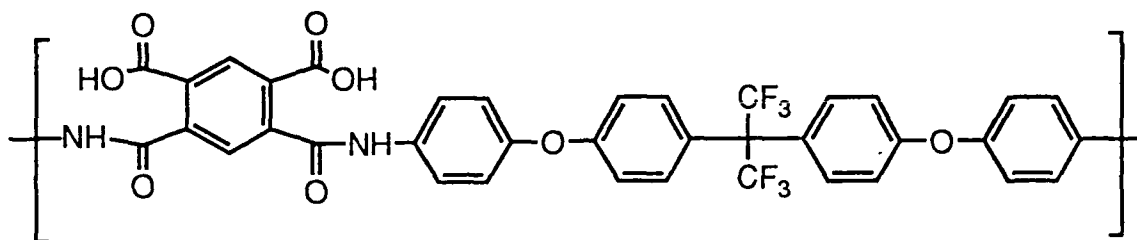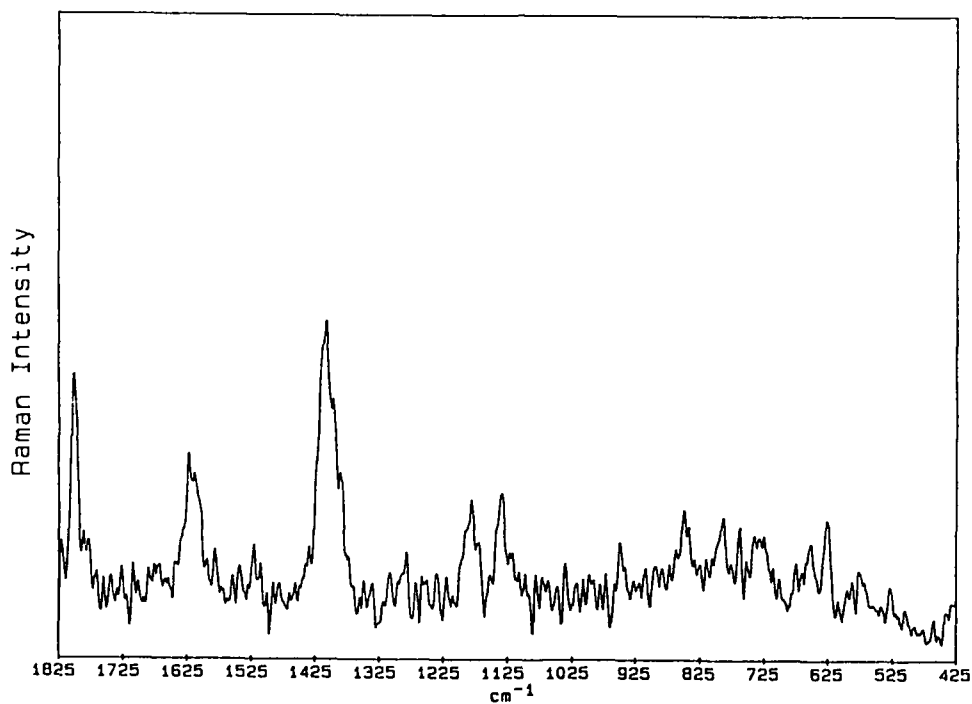
(A)
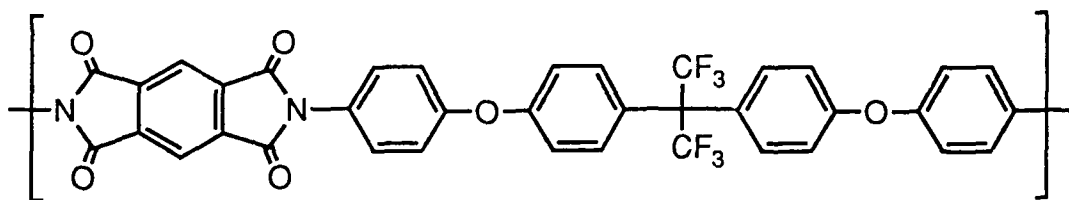
(B)

Figure 1. Molecular structures of the (A) – polyamic acid and
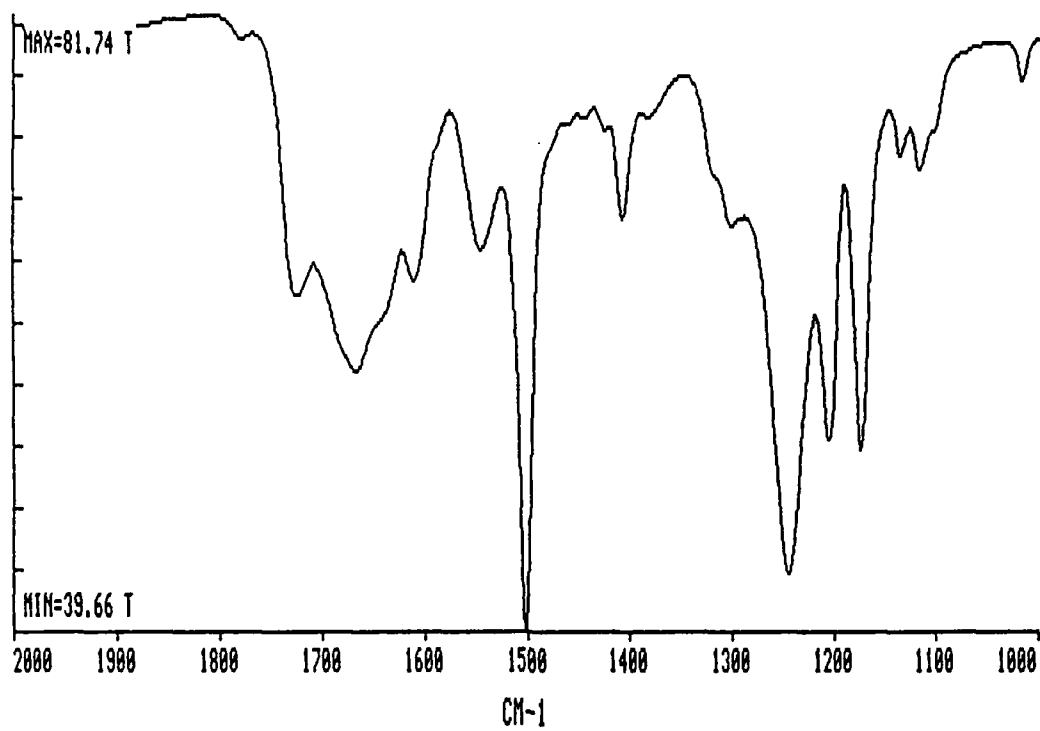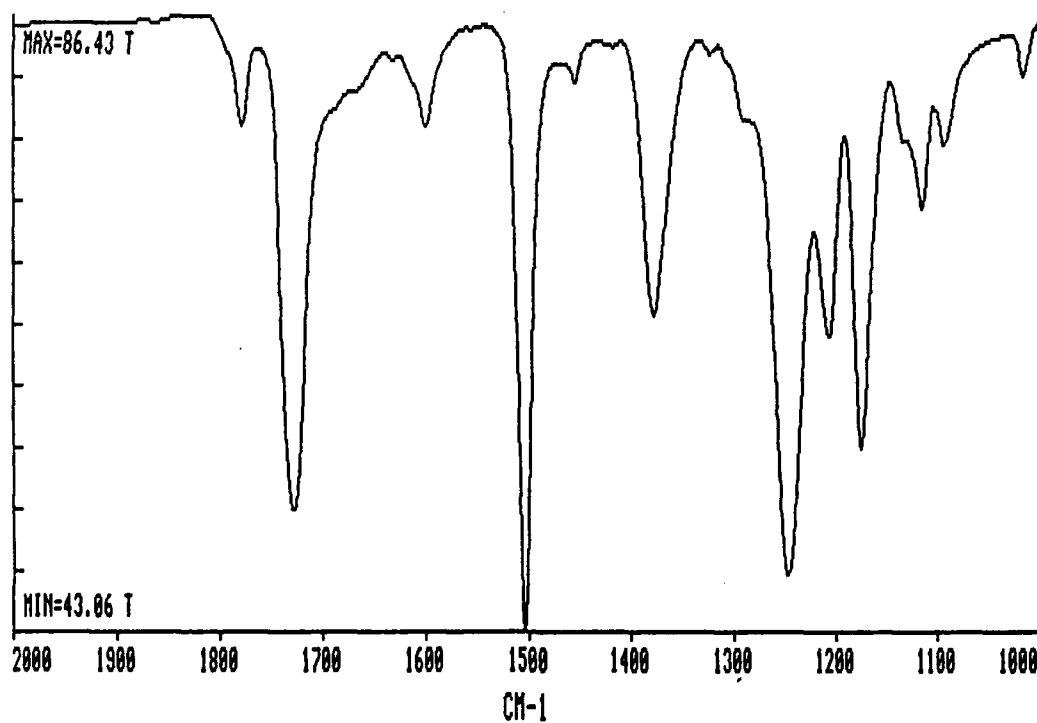(B) – polyimide of PMDA/4-BDAF.
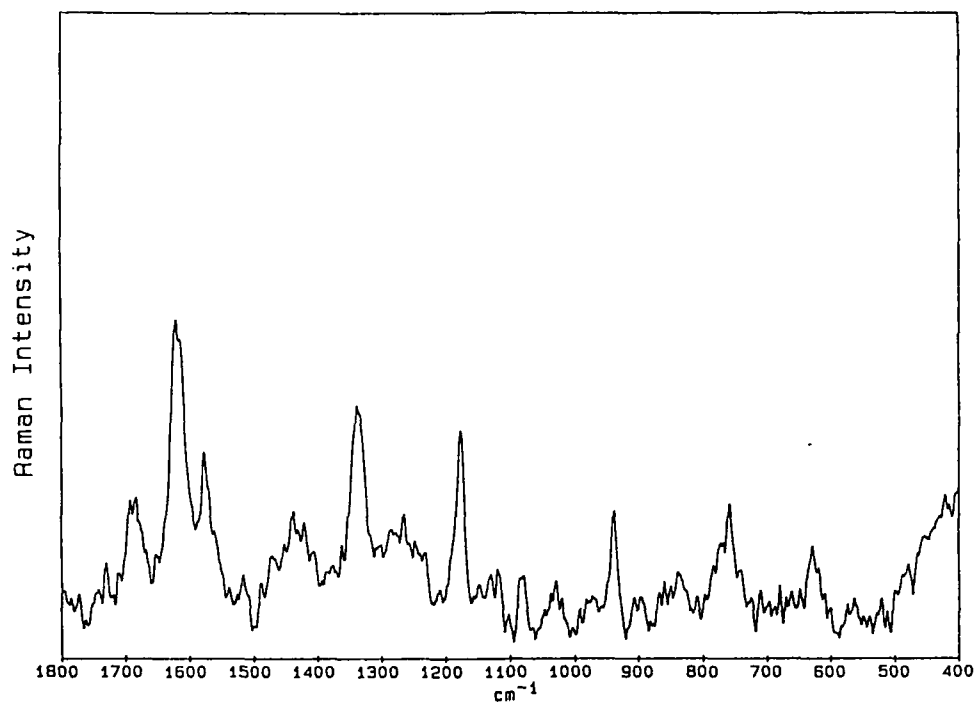
(A)

(B)

Figure 2. Normal Raman spectra of the (A) - polyamic acid and
(B) - polyimide of PMDA/4-BDAF.

Figure 3. Transmission infrared spectra of the polyamic acid of PMDA/4-BDAF (A) - before and (B) - after curing.

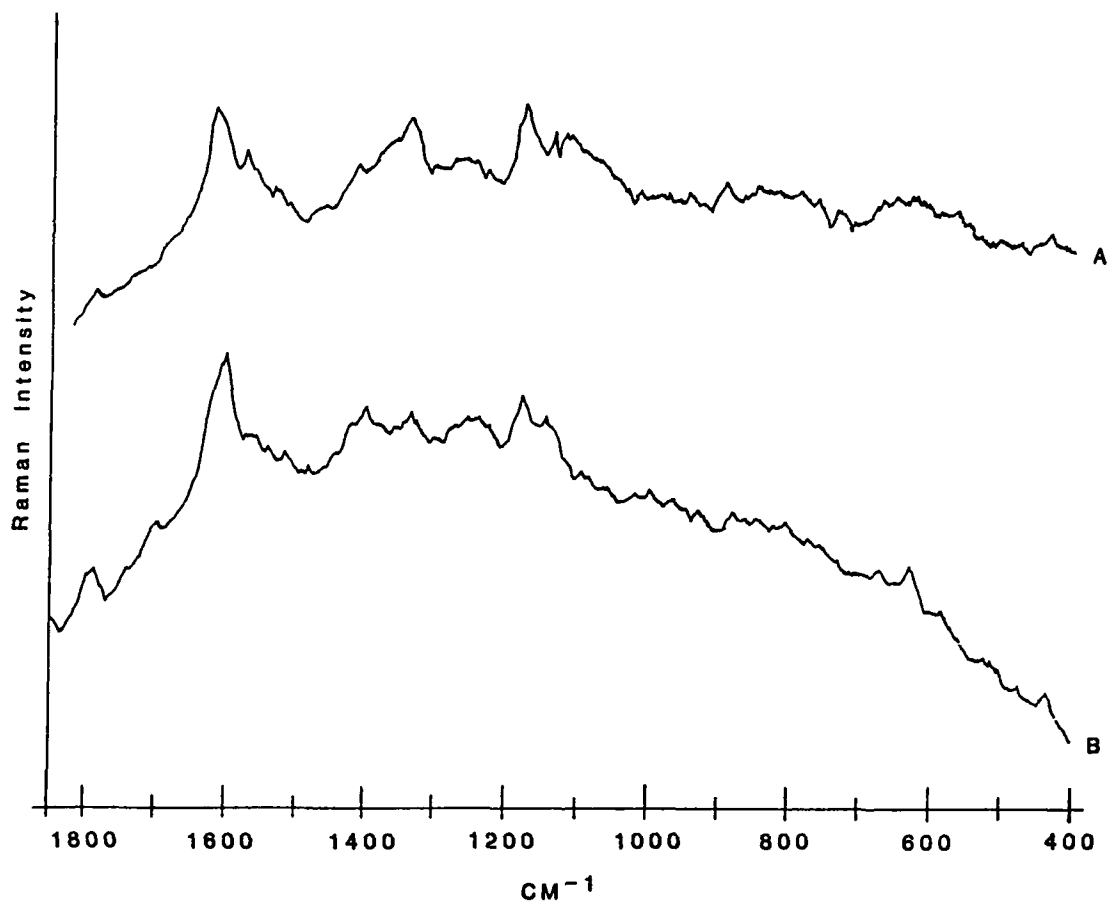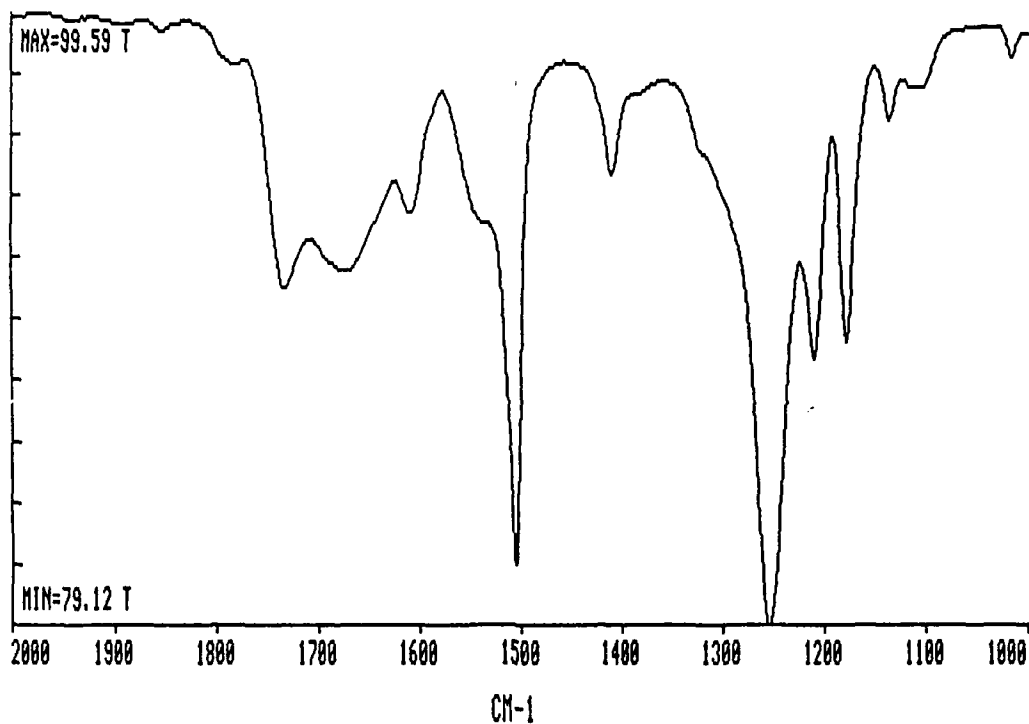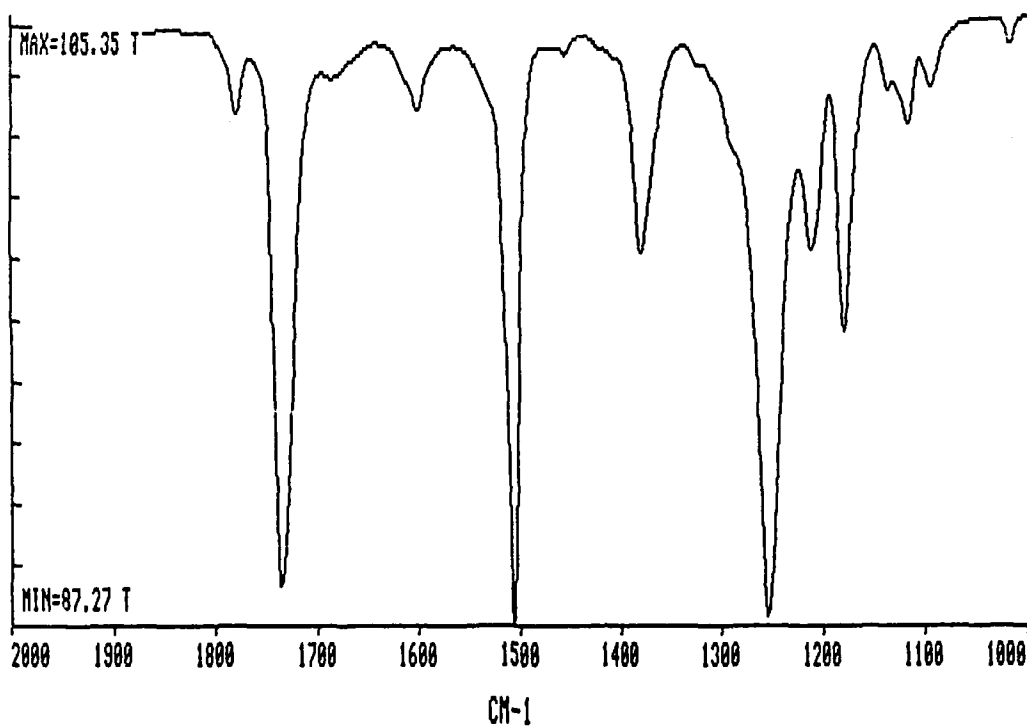Figure 4.   SERS spectra of the (A) - polyamic acid and (B) -
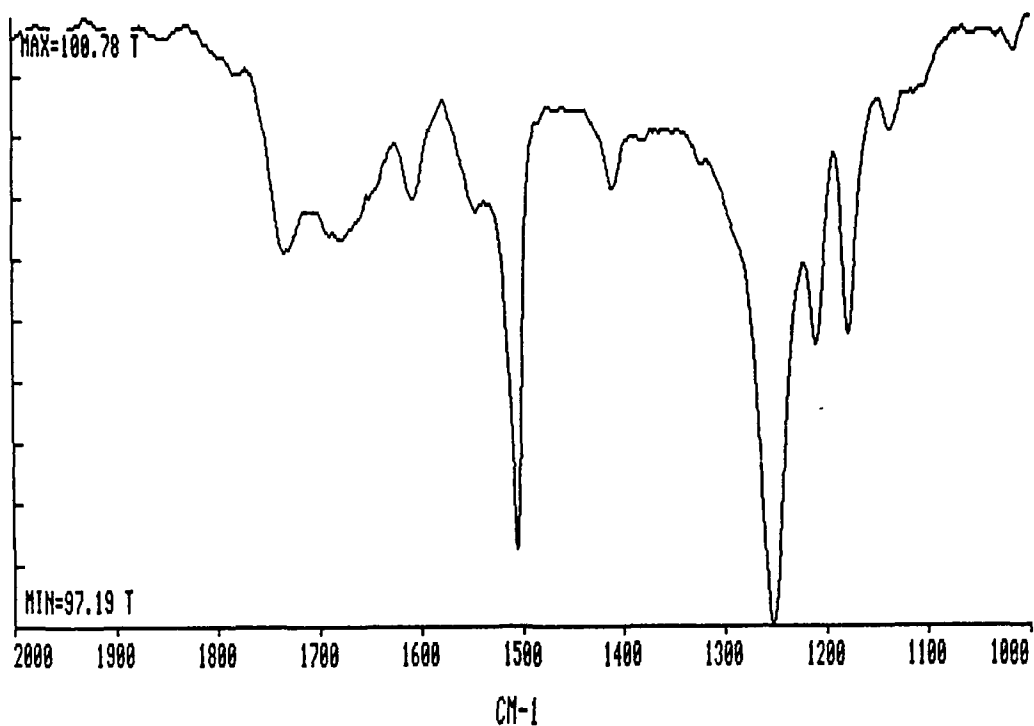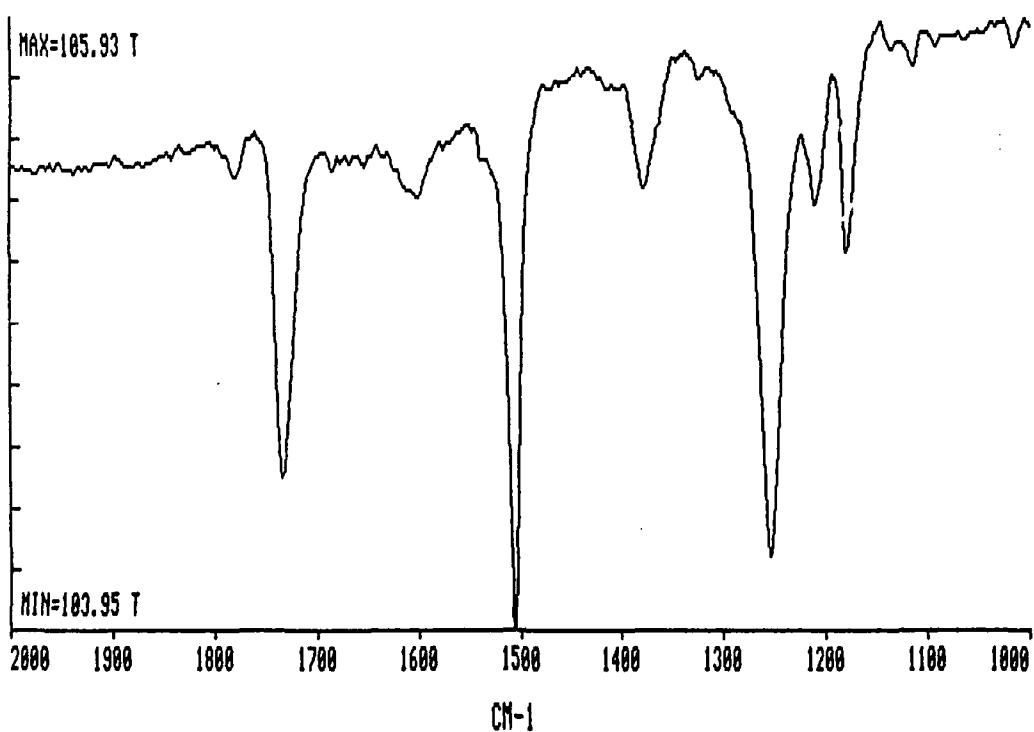   polyimide of PMDA/4-BDAF.

Figure 5.   Reflection-absorption infrared spectra obtained from
thin films of the polyamic acid of PMDA/4-BDAF spin-
coated onto thick silver films from a 5% solution in
N-methylpyrrolidone (A) - before and (B) - after
curing.

Figure 6. Reflection-absorption infrared spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF spin-coated onto thick silver films from a 1% solution in N-methylpyrrolidone (A) - before and (B) - after curing.
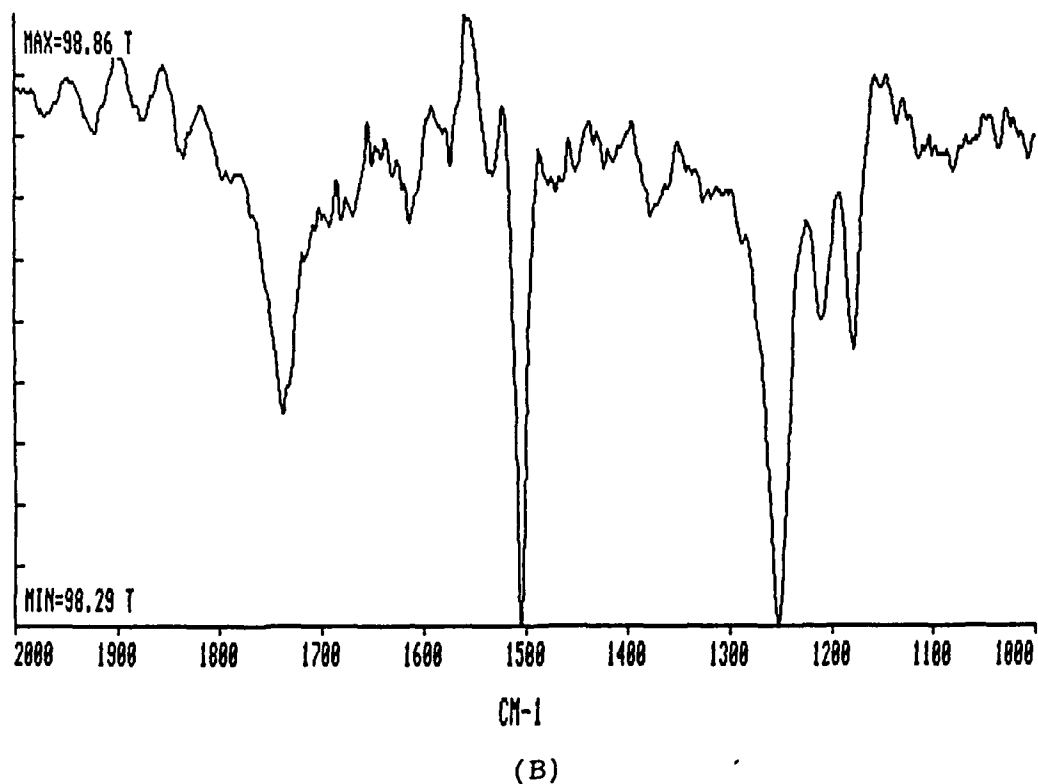
(A)

(B)

Figure 7.   Reflection-absorption infrared spectra obtained from thin films of the polyamic acid of PMDA/4-BDAF spin-coated onto thick silver films from a 0.2% solution in N-methylpyrrolidone (A) - before and (B) - after curing.
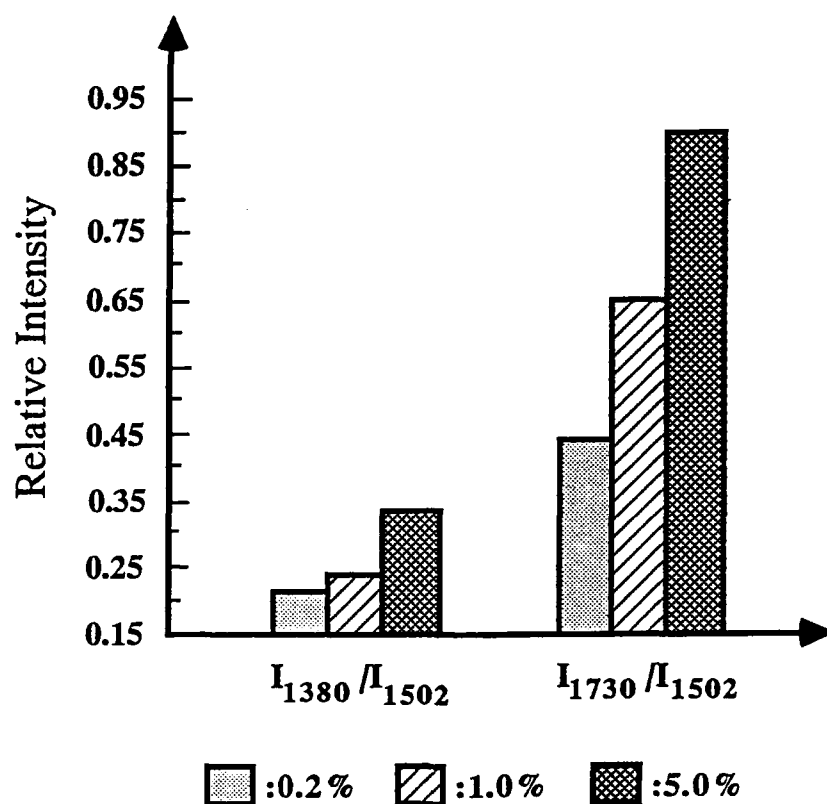
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Figure 8.   Intensities of the bands near 1380 and 1720 cm^{-1} in the RAIR spectra of PMDA/4-BDAF films relative to that of the band near 1502 cm^{-1} as a function of the concentration of the solutions from which the films were deposited.

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